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Electron transport through single gold atoms and hydrogen molecules switching on the atomic scale

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Chapter 7

Two level fluctuations in hydrogen affected gold tunnel junctions

Abstract

In this chapter, conductance measurements on gold tunnel junctions are presented, in a hydrogen environment. Right after the addition of the hydrogen molecules, two level fluctuations (TLF) appear in the tunneling regime. These TLF are attributed to hopping of a molecule in between two positions, a process which is triggered by inelastic excitations of the molecule. Furthermore, we show that the potential landscape can be changed by varying the electrode separation. Hence, we can control the preferential conductance state in two ways: by vibrational heating and by tuning the electrode interaction.

7.1 Introduction: two level fluctuations

In the previous two chapters, we showed that a hydrogen-gold junction can heat up, at voltages above the vibration energy of the hydrogen molecule. This resulted in a change in conductance, which was attributed to a two level system where the molecule hops in between two different configurations in the contact. However, the two level fluctuations (TLF) were generally faster than the bandwidth of our electronics, leading to an apparently smooth transition to the other conductance

This chapter is based on Ref. 5 on p. 147

level. In this chapter, we present our results on hydrogen-gold junctions where the electrodes are separated by a tunnel gap. The hydrogen molecule is now not contacted, but adsorbed on the gold electrodes. Interestingly, in comparison to the case where the molecule is contacted, the two level fluctuations are now slower and can be resolved in time. A typical example is plotted in Fig. 7.1. Clear two level fluctuations are observed in the current, with an amplitude up to 100 %. Since these fluctuations are time-resolved, we have the opportunity to quantitatively investigate the two level system. By systematically changing the voltage and the electrode distance, we gain information on the exact physical mechanism of the TLF.

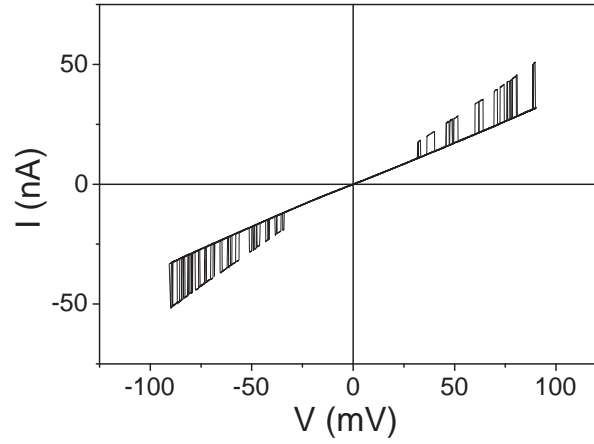


Figure 7.1: *IV measurement on hydrogen covered gold electrodes, separated by a vacuum gap. Clear two level fluctuations can be observed above 30 mV. $V_{in}=0.1$ Hz.*

7.2 Experimental details

For our measurements on the hydrogen affected tunnel junctions, we use a similar experimental method as described in the previous two chapters (see section 5.3). However, we now focus on junctions which are separated by a tunnel gap. The experimental details are as follows: To start with a clean gold system, the wires are cooled down to 4.2 K, after which the electrodes are broken. This gives clean gold electrodes, in cryogenic vacuum. The cleanliness of the electrodes is checked by measuring IV curves, real time, by sweeping the voltage each second from -200 to +200 mV, resulting in a smooth tunnel curve. Next, a small amount

of high purity hydrogen gas (99.999 %) is brought into the insert ($\approx 1 \text{ cm}^3$, 1 mbar), although higher quantities lead to similar results. Within 5 minutes after admission of the hydrogen, two level fluctuations start to appear in the IV curves measured in the tunneling regime.

7.3 Two level fluctuations as a function of bias voltage

7.3.1 Inversion of the ground state

Let us return to Fig. 7.1. Clearly, the observed two level fluctuations strongly depend on the applied bias voltage. Below 30 mV no fluctuations are observed, whereas at higher voltages, the current starts to fluctuate in between two different conductance levels, with increasing frequency. However, besides the increasing frequency, also the occupation of the two conductance levels changes. This effect especially shows up in Fig. 7.2(a). With increasing voltage, the conductance of the system gradually changes from the high conductive state (with conductance σ_0) to the low conductance state ($G = \sigma_1$). Interestingly, we can use these plots to calculate the actual (fractional) occupation of each state. For a given bias voltage, the time-averaged conductance ($\bar{\sigma}$) is a function of σ_0 and σ_1 , and can be described by:

$$\bar{\sigma} = n_0\sigma_0 + n_1\sigma_1 \quad (7.1)$$

where n_0 and n_1 are the fractional occupation numbers of the high and low conductance state respectively (note that $n_0 + n_1 = 1$). This gives us the opportunity to directly calculate the fractional occupation numbers, as a function of voltage. The result is plotted in Fig. 7.2(b). At bias voltages below 25 mV, the system is completely in the ground state ($n_1 = 0$). At higher voltages, the system slowly saturates to the lower conductance state. Apparently, the occupation of the conductance states strongly depends on the applied bias voltage, and can be completely inverted for low and high bias voltages. Furthermore, the sudden onset of the TLF indicates a vibrational level around 30 mV (we will return to this observation in the next section).

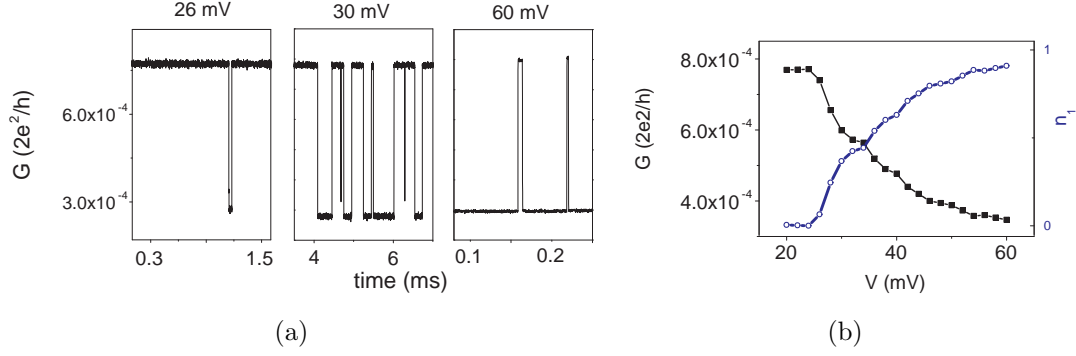


Figure 7.2: (a) Conductance of a tunnel contact as a function of time, for 3 different voltages. The average conductance of the system changes in between 30 and 60 mV, from the upper to the lower conductance level. (b) Conductance and fractional occupation of the excited state, as a function of bias voltage. The fractional occupation of the lower conductance level slowly changes from 0 (at $V < 25$ mV) to a value close to 1 at voltages > 60 mV.

7.3.2 Transfer rates

A second method to characterize the TLF, is to investigate the residence times of each conductance level. When we assume that the two levels are independent and have no memory, the residence time probability density $P_{0,1}$ is given by a two state Markov process [2].

$$P_{0,1}(t) = R_{0,1} \exp(-R_{0,1}t) \quad (7.2)$$

where $R_{0,1}$ is the transfer rate of the specific conductance state. The residence time distributions for the two conductance levels, can indeed be well described by an exponential distribution, as shown in Fig. 7.3.

Subsequently, by repeating the analysis for different bias voltages, one can plot the transfer rates as a function of bias voltage. An example is plotted in Fig. 7.4(a). Interestingly, the transfer rates seem to follow a power law with the applied bias voltage. As we will show in the next section, this is a strong indication that the process is triggered by inelastic excitations of the molecule [1].

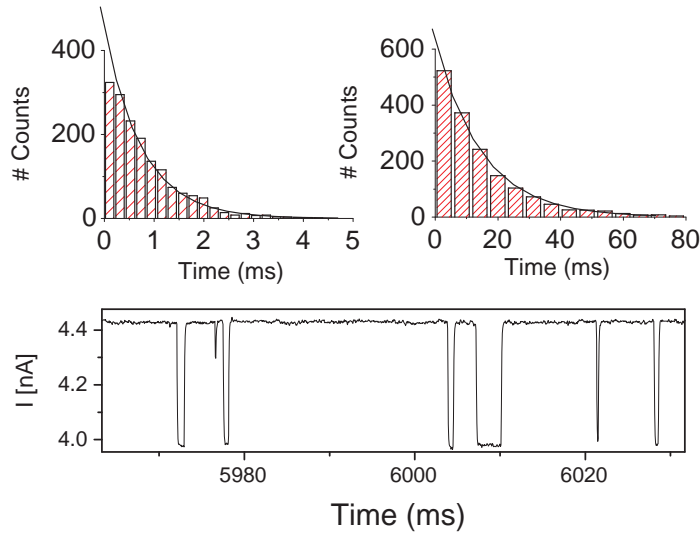


Figure 7.3: Two level fluctuations, as a function of time. Lower graph: Current as a function of time, for $V=90$ mV. Sample rate is 20 kHz with an averaging time of $50 \mu\text{s}$ for each data point. Upper graphs: statistics of the residence times for the lower and upper conductance state respectively for the measurement plotted below (For the histogram, the current is recorded for 25 seconds). The line is a fit with a single exponential function.

7.3.3 Vibrational heating model

One of the first atomic two level systems described in literature, is the xenon switch, as published by Eigler *et al* [3]. Here, a xenon atom could be reversibly switched between the STM tip and surface, by applying a voltage pulse. The transfer rates of the Xenon atom, were found to have a power law dependence on the current. To explain this result, a vibrational heating model was proposed, where an atom can overcome an energy barrier by multiple inelastic excitations [4, 5, 6]. This model is schematically drawn in Fig. 7.5, and is widely used for explaining two level fluctuations in molecular electronics [7, 8, 9, 10]. Basically, the model states that the energy of an atom or molecule can stepwise increase by vibrational excitations taking up energy from tunnel electrons. Thus, the molecule can climb a vibrational ladder, with probability Γ_{\uparrow} (thereby taking up energy equal to $\hbar\omega$). Subsequently, by releasing energy to electrons or to substrate phonons, the molecule can step down in energy with probability Γ_{\downarrow} . This results in a probability R_n to reach the highest level n :

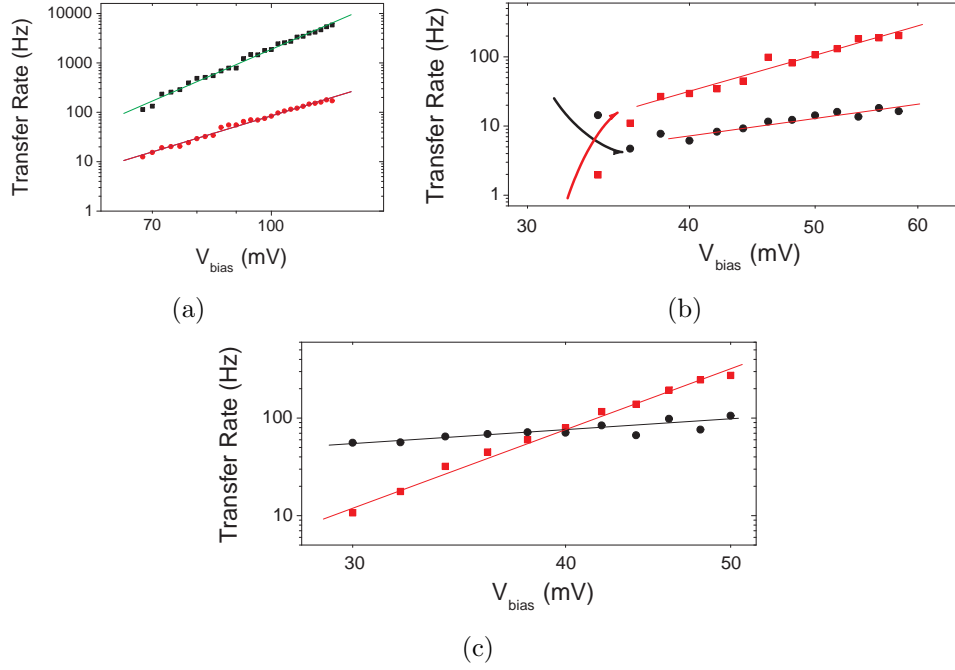


Figure 7.4: Transfer rates as a function of bias voltage, for two different contacts (including linear fits). (a) Same contact as depicted in Fig. 7.3. Slopes of the lines are 6.7 and 4.7 for the upper and lower line respectively. (b) Transfer rates for the same contact as discussed in Fig. 7.2. Note the inversion of the ground state, around 35 mV. Slopes are 2.6 and 5.4. (c) transfer rates of the contact shown in Fig. 7.5(b), after stretching ≈ 8 pm. The most preferential conductance state changes around a bias voltage of 40 mV. Slopes are 1 and 6.3.

$$R_n \simeq n\Gamma_{\uparrow} \exp\left(-\frac{(n-1)\hbar\omega}{k_B T_v}\right) \quad (7.3)$$

where $\hbar\omega$ is the vibration energy, k_B is the Boltzmann constant, and T_v is the vibrational temperature. Furthermore, when the atom or molecule reaches the highest level n , it has enough energy to cross the energy barrier, and hop to another position (to the other potential well). As depicted in Eq. 7.5, the transfer rate for barrier crossing strongly depends on the vibrational temperature T_v , which is given by:

$$T_v = \frac{\hbar\omega}{k_B \ln \frac{\Gamma_{\downarrow}}{\Gamma_{\uparrow}}} \quad (7.4)$$

Combining these two equation results in the following expression for the transfer rates:

$$R_n = n\Gamma_{\uparrow} \left(\frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow}} \right)^{n-1} \quad (7.5)$$

Furthermore, by calculating the excitation and deexcitation rates, one finds that the ratio $\Gamma_{\downarrow}/\Gamma_{\uparrow}$ is a function of the number of injected electrons [5]. This results in a transfer rate proportional to I^n . Finally, since we are in the Ohmic regime of tunneling (voltage is much smaller than the workfunction of gold), the voltage is proportional to the current. Hence, we can write $R \propto V^n$, resulting in a power law dependence of the transfer rates, as a function of voltage.

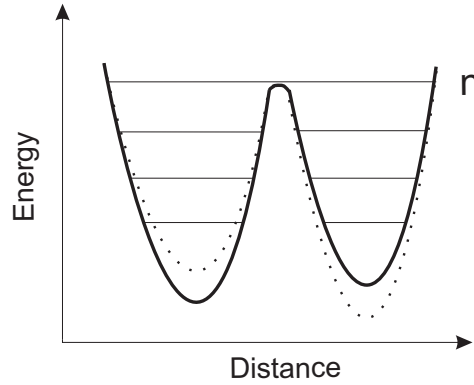


Figure 7.5: *Vibrational heating model. The molecule can overcome the barrier by stepwise climbing of the vibrational ladder. After n excitations, the molecular energy is higher than the energy of the potential barrier (solid line, with $E = n\hbar\omega$), and the molecule can cross the energy barrier. Dotted line: By changing the electrode separation, the potential landscape changes, thereby changing the ground state of the two level system.*

The power law is consistent with our observations, as plotted in Fig. 7.4. Hence, this indicates that the TLF are triggered by inelastic excitations of the hydrogen molecule. This is as expected, since the TLF are perfectly symmetric in the voltage, just like the observed heating effect at the hydrogen vibration frequency for contacted hydrogen molecules (as discussed in chapter 5). In this context, Fig. 7.4(b) is an important result. At voltages higher than 40 mV, the transfer rates follow the expected power law dependence on the voltage. However, a strong deviation from the power law is observed around 35 mV. Here,

the ground state suddenly changes from the high conductance state to the low conductance state. Interestingly, 35 mV is close to the typical vibration energy of contacted molecular hydrogen (around 40 mV). Hence, this graph shows the onset of the vibrational heating. Note that a similar onset around 30 mV is observed for the contact depicted in Fig. 7.2(b).

However, we emphasize that the vibrational heating model does not give a complete description of our observations. First of all, the model predicts that the slope of the power law equals the number of vibrational levels in the well. However, we observe strong differences in the slopes of power law for the upper and lower conductance states (as for Fig. 7.4). This would insinuate a strong difference in depth of the two potential wells. In contrast, the balance equation states that $R_1/R_2 = \exp[-(E_1 - E_2)/kT]$, where E_1 (E_2) is the depth of the potential well for state 1 (2). Thus, a crossing of the transfer rates for the upper and lower level would indicate that the depth of the potential well depends on the applied voltage. This is inconsistent with the linear slopes of Fig. 7.4(c). Hence, a more advanced theoretical model is needed for explaining our observations. We note here the calculations done by Halbritter *et al*, to explain the negative differential conductance as observed for contacted hydrogen molecules (as discussed earlier in section 5.2.2). They suggested a strongly asymmetric system for the two different conductance levels [11]. Our data presented in this section give new insight in this discussion.

7.4 TLF as a function of electrode distance

Finally, we investigate the TLF by changing the electrode separation. It is well known that the binding forces between the opposing atoms can have a large influence on the potential landscape around the apex [2, 12, 13]. Remarkably, these attractive forces can even change the fractional occupation of the two different conductance levels. A first example is plotted in Fig. 7.4. For Fig. 7.4(b), the inversion of the ground state occurs at a bias voltage of around 35 mV. However, by increasing the electrode separation by only 8 pm, the position of the ground state inversion shifts towards 40 mV. This effect is even more pronounced for the contact depicted in Fig. 7.6. Here, the conductance is measured at a bias voltage of 100 mV (well above the vibration energy of the molecule). By changing the electrode separation by 160 pm, the preferential conductance level is completely inverted. This process is schematically drawn in Fig. 7.5. By using the attractive

forces of the electrodes, one can change the potential landscape, and even change the ground state of the system (dotted line). We note here that a very similar effect was observed by Strosio *et al*, where they investigated the dynamics of a Co atom on a Cu surface (using an STM) [2]. Also here, a TLF system was observed, where a Cu atom hopped back and forth between two lattice positions. By changing the electrode separation (and so the electrode interaction), one could strongly change the potential landscape, and even "select" the preferential conductance level.

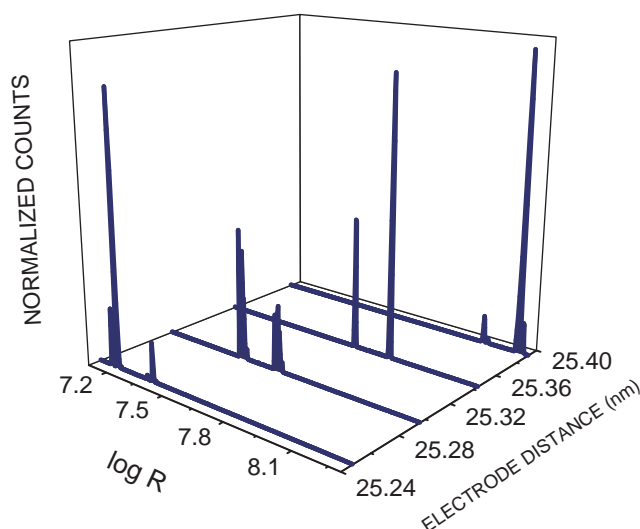


Figure 7.6: Histogram of resistance values of TLF as a function of electrode distance. By decreasing the electrode separation by ≈ 160 pm, the fractional occupation is completely inverted. For close electrode separations, the low resistance level is now preferred above the high resistance level. Measurement taken with a bias voltage of 100 mV.

7.5 Comparison with measurements on contacted molecules

In Fig. 7.2 and Fig. 7.4(c) a gradual transition towards another conductance level was observed, at increasing voltage. A similar transition was observed for contacted molecules (as discussed in chapter 5). However, for the contacted molecules, the complete transition occurred within a much smaller voltage window (< 5 mV), and the two level fluctuations were too fast to be resolved in time.

Furthermore, for the contacts discussed in this chapter, the onset of the TLF occur at voltages anywhere above 30 mV, while this is more restricted for the contacted molecules ($30 < V < 50$ mV). We suggest here that this could be related to a smaller energy barrier when the molecule is contacted between two electrodes. For larger energy barriers (for tunnel junctions), a higher vibrational temperature (and higher voltage) is needed for complete inversion of the conductance level. In contrast, for small energy barriers, a complete cross over to another conductance level can already occur right after the first inelastic excitations (at $V = \hbar\omega/e$). An example of a contact in the intermediate regime (contacted or tunnel junction), is plotted in Fig. 7.7. Here, the cross over to a higher conductance level occurs within 20 mV, while still two level fluctuation can be observed. Also, a hysteresis effect shows up, of the same time scale as discussed in chapter 5.

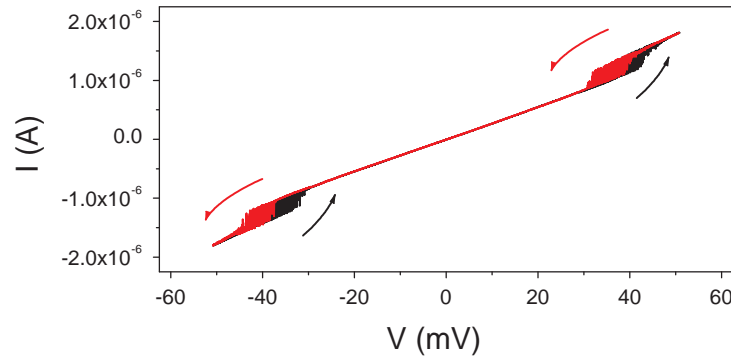


Figure 7.7: *TLF fluctuations at relatively high contact conductance of $0.3 G_0$. The trace for increasing voltage is plotted in black, the trace for decreasing voltage in red/grey. The cross-over to the higher conductance level occurs in between 30 and 50 mV. The voltage is swept in 1 Hz. Note the hysteresis between the trace and retrace, of a ms time scale.*

7.6 Conclusions

To conclude, we have performed conductance measurements on gold tunnel junctions, in a hydrogen environment. Well resolved two level fluctuations are observed, which are attributed to hopping of a hydrogen molecule in between two different positions on the gold electrodes. The transfer rates were found to have a power law dependence on the voltage, which is indicative for vibrational heating. Moreover, the observations are independent of the polarity of the voltage,

thereby excluding any electromigration effects. Furthermore, the most preferential conductance level was found to be strongly dependent on both the voltage and electrode separation. Hence, our results give new insight in vibrationally induced two level fluctuations.

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